

Soft Condensed Matter (Materia Condensata Soffice)

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Abstract. This article was written for a multi-volume History of Science, and published in Italian translation: *Storia della Scienza*, Volume IX, *La Grande Scienza*, pp 645–656 (Published by Istituto della Enciclopedia Italiana, Fondata da Giovanni Treccani, 2003). In it, I describe the evolution of soft matter physics as a discipline during the 20th century.

Introduction

Soft condensed matter physics concerns colloids, polymer solutions, emulsions, foams, surfactant solutions, powders and similar materials. (Domestic examples are respectively paint, engine oil, mayonnaise, shaving cream, talc, etc..) In each case, the precise molecular composition of the system has only limited influence on the physical behaviour, which is controlled by structure on the mesoscopic scale (between, say, one nanometre and one micron) that is easily reorganized by external influences such as mechanical stress. The unusual mechanical properties of such soft condensed phases are widely exploited both by nature and by mankind, either directly or during processing. An example of the latter is the moulding of a hard plastic object by casting it from the melt: polymer melts represent soft condensed matter ‘par excellence’.

Intellectual and Social Context

The second half of the 20th century, and especially its final two decades, saw a very strong growth in our understanding of soft condensed matter physics. Several reasons for this can be identified.

Firstly, there have been a number of industrial drivers for research in this field. Indeed, the wide availability of well-controlled synthetic samples of polymeric and colloidal materials dates back only to the 1940s and 1950s, and can be viewed as a by-product of the emergence, at about that time, of the plastics industry. Before this, studies were reliant on naturally occurring materials (such as natural rubber) and/or ones with relatively poor reproducibility. From the 1950s onwards, the industrial motivation for an improved understanding of the physical properties of polymers was clear. There were several other industrial drivers, such as the increasing transfer (from the 1960s onwards, at least in western countries) of food preparation duties from the kitchen to the factory. This required a far more scientific approach to understanding the mechanical stability of soft materials. Subsequently, mounting environmental and health concerns have maintained this pressure. For example, paints and coatings which used to contain harmful organic solvents are now mainly water-based; many foods that used to contain chemical preservatives or artificially hydrogenated fats no longer do so. In many such cases, it is the better application of physics (the control of structure by mechanical or thermal processing) that allows less reliance on chemical methods of stabilizing a product.

Setting aside these industrial motivations, soft condensed matter has benefited greatly from broader scientific developments. Much progress has stemmed from improved experimental methods, particularly the use of scattering by laser light, X-rays and neutrons as probes of static and dynamic structure. Laser light scattering (which stemmed from the invention of the laser itself in the late 1950s) has proven particularly valuable because the length scales probed by it are suitable for exploring mesoscopic structure; the dynamic version, in which the object of study is the time correlation of the scattered intensity, allows detailed characterisation of motion on the micron scale. From the 1980s onwards, the power of such methods was extended further through the development of techniques to allow interpretation of laser light scattering data from turbid or even opaque materials.

Of comparable importance to these advances in experimental methods was the emergence of computer simulation as a reliable tool. The first simulations of hard-sphere liquids (effectively, colloids) were done in the late 1950s, with serious work on

polymer statistics initiated in the 1960s; on polymer dynamics in the 1970s and 1980s; and on self-assembly in the 1980s and 1990s. All these fields have, alongside many others, fed on the growth in computational power available. However, even today, many important issues in soft condensed matter are too complex to be resolved by computer simulation alone.

A final reason for strong progress in soft condensed matter was the development of improved theoretical methods based on advances in statistical mechanics. Some of these were general and far-reaching, such as the scaling and renormalization-group techniques for studying phase transitions which emerged in the 1960s and 1970s (see Chapter 10). Other theoretical developments, such as the tube model of polymer entanglement (described below) were devised for specific problems in soft matter and had neither precedent nor analogue in other fields of physics. Throughout the second half of the 20th century, by a judicious combination of general and specific theoretical methodologies, an increasing number of physical properties of soft condensed matter thus came to be explained, or even quantitatively predictable, in terms of a few unifying concepts such as entropic elasticity and Brownian motion. Indeed, from the early studies of the 1940s and 1950s to the present day, soft condensed materials such as colloids and polymers have offered an important testing ground for emerging ideas in statistical mechanics. This symbiosis between soft matter experiment and statistical mechanics theory is a recurrent theme in what follows.

Condensed Matter Physics

Condensed matter physics addresses the behaviour of systems containing very many particles, at high enough density that each interacts with several others. Examples include crystalline solids and liquids. Because each atom or molecule interacts with several neighbours, and each of these with several more, and so on, the entire system of particles is coupled together. This imparts special ‘collective’ properties to the material, such as the elasticity of a crystal, or the viscosity (thickness, resistance to flow) of a liquid. Such properties cannot usually be understood by thinking about single particles in isolation, or even small clusters of particles; condensed matter physics is, in essence, ‘the 10^{23} body problem’.

During the first half of the 20th century, tremendous progress was made in the study of condensed phases, such as regular crystalline solids, by applying the (then) newly-discovered laws of quantum mechanics to periodic assemblies of atoms. This work continues today, with ever more sophisticated techniques being employed (see Chapters 11.1, 11.2, 11.5). Quantum mechanics alone was not enough, however. For example, the understanding of magnetism in solids required not just quantum theory but also the tools of statistical physics. These are the rules which allow one to calculate the probability that a many-body system is in a particular microscopic physical state (a specific quantum state, or ‘microstate’) at a given temperature. The collective properties of a condensed phase are then expressed as averages over this probability distribution. Sometimes abrupt changes in these properties can result from small changes in control parameters such as temperature; when the abrupt behaviour becomes ever more singular as the thermodynamic limit (of large system sizes) is taken, such phenomena are called phase transitions (See Chapter 10).

Because, in thermal equilibrium, a large system explores many microstates, its behaviour depends on how many of these microstates there are in any given energy range, as well as the physical character of the microstates themselves. For example, the

fact that a ferromagnetic material (spins on a lattice) entirely loses its magnetization when heated above a critical temperature (the Curie temperature) is understood qualitatively as follows. At low temperature, the system remains in energy states of low energy E , all of which are magnetized (the spins, on average, are aligned along a common axis). At high temperature, the system samples states more widely ranging in energy, the vast majority of which are not magnetized (unaligned). The disappearance of magnetization marks the victory of the tendency to maximize the entropy S (which is, quantitatively, the logarithm of the number of microstates that the system can sample) over the tendency to minimize energy. (The magnetization vanishes smoothly at the phase transition point but its functional form changes there, so that – for example – its temperature derivative is discontinuous.)

This basic competition is quantified in the celebrated formula of Hermann von Helmholtz (1821-1894) for the free energy

$$F = E - TS \quad (1)$$

The thermodynamic state of equilibrium at temperature T in a system of fixed contents (and fixed volume V) is the one that minimizes F . This represents a concise statement of the laws of equilibrium statistical mechanics as conceived by Ludwig Boltzmann (1844-1902) and Josiah Willard Gibbs (1839-1903). Late 20th century research, for example in disordered magnetism, has continued to explore the conflict between energy and entropy, revealing a battlefield of surprising complexity (see Chapter 11.3).

Equally vital has been the issue of dynamics – how does a many body system approach its equilibrium state? Can it get trapped away from equilibrium? What happens if the system is constantly being “driven” by an input of energy from outside? These issues are among those discussed, in more specific contexts, below.

Soft Condensed Matter

We now turn specifically to soft condensed matter. First, what is it? There is no agreed definition, but one candidate is as follows: a piece of soft condensed matter is a lump of material which strongly resists compression, but weakly resists shear. An example is a piece of crosslinked natural rubber (latex); this is can easily be deformed at constant volume but, perhaps surprisingly, its resistance to changes in volume (its bulk modulus) is as high as many a crystalline solid. The following materials thus qualify as soft condensed matter: polymer gels (Jello), emulsions (mayonnaise), viscoelastic detergent solutions (shampoo), fat crystal networks (margarine), concentrated colloids (paint), polymer solutions (multigrade engine oil) and lyotropic liquid crystals (such as the slime created when a bar of soap is left in a pool of water). Less obvious qualifiers are shaving foam and beer froth, which are also relatively incompressible so long as the trapped gas is not allowed to escape.

Dense colloids (e.g. the thick paste made by mixing cornstarch with water) also qualify. These can develop high resistance to shear under strong stresses (a phenomenon called shear-thickening behaviour) but are nonetheless easier to shear than to compress. The case of dry powders is slightly anomalous – such powders can fill a range of different volumes depending on how the sample has been shaken. (This is why a packet of cornflakes is always less full by the time it reaches the shop than when it left the factory.) Powders also tend to expand on shearing (dilatancy). Hence they do not fit easily into the definition chosen above but are traditionally part of

the remit of soft condensed matter, in part because much of their behaviour is closely similar to that of dense colloids.

How do all these materials differ from simple liquids, such as water? The latter is not easily compressed, and, it could be said, weakly resists shear. But it does so in a purely viscous manner: the force generated is proportional to the rate of strain. (This is called ‘Newtonian’ behaviour after Isaac Newton (1642-1727), who first described it.) In contrast, most of the above materials are ‘viscoelastic’: their response to deformation shows a mixture of elastic and viscous features. For example a polymer solution, to which a small shearing force is applied, will first respond elastically – it will deform with a shear strain linear in the applied force per unit area (the shear stress). But after a finite time (perhaps a second or two, or much longer in some cases), it will start to flow like a liquid – with a strain rate (not strain) proportional to the stress. Thus arise various entertaining toys such as ‘silly putty’, which bounces like a rubber ball, but, if left alone, will spread to form a thin pancake (which is actually a puddle) on the table. The first person to consider such behaviour theoretically was James Clerk Maxwell (1831-1879), who invented a simple theoretical description for it (now known as the Maxwell model).

The distinction made above is based on time-scales: water too responds elastically at first, but so briefly that most experiments do not detect this. The soft materials of interest here instead show some degree of elasticity on time scales (milliseconds to days) that are readily observed. Note that many soft materials, including all the examples in the list above, do consist mainly of a simple fluid – such as water – in which ‘mesoscopic’ objects are suspended. Such objects have structure on the nanometre to micron scale, and their slow dynamics prolongs the elastic response. Polymers (long chain molecules) or colloidal particles (spherical or irregular lumps of hard matter) are important examples. In both these cases, the suspended objects are permanent in character: unless extreme conditions are applied, they remain intact throughout the life of the material. Other cases, in which the suspended objects are transitory, are considered later.

Thermal Equilibrium

A major achievement of the late 20th century was to understand, at least at a schematic level, the equilibrium statistical mechanics of key soft materials including polymer solutions and colloidal suspensions. In many interesting cases, the physics is dominated by the entropic term in Eq.1.

Polymers

For example, a linear polymer chain is a long, unbranched sequence of chemically identical units, connected by bonds with some flexibility. Such a chain can be viewed, at a large enough scale, as simply a wiggly line: there are a vast number of microstates (corresponding to different sequences of configurations of bonds in the chain) whose energies are not very different from one another. The details of the local chemistry do not matter in this limit: the polymer’s properties become ‘universal’. Under these conditions, what matters in Eq.1 is the maximization of entropy; each chain becomes a random walk. A random walk is a path, made up of a sequence of steps, each taken in a random direction relative to the previous one. A picturesque example, in two dimensions, is the trail of a drunkard staggering away from a public bar, with no

notion of where he has been or where he is going. The path traced out by a polymer, now in three dimensions, is similar – with the important proviso that no two parts of the same chain, or of any two chains, can be in exactly the same place. The detailed effect of this ‘excluded volume’ constraint on chain statistics is subtle but the main effect is to make the chain expand to fill a larger region of space.

Notice that any individual polymer is constantly exploring its vast number of microstates (by Brownian motion – see below); few meaningful properties can be defined except as an average over this exploration. This is very unlike the atoms or molecules in a conventional ‘hard’ material, such as iron, where the entropic fluctuations can be viewed as small departures (called phonons) from a well-defined ground state (the periodic lattice). For polymers, as is commonplace in soft condensed matter, the fluctuations are the physics. This makes the correct use of statistical mechanics especially challenging, and especially important.

Many advances in understanding polymer statistical mechanics were made by Paul J Flory (1910-1985; Chemistry Nobel Prize 1974), Pierre-Gilles de Gennes (b.1932; Physics Nobel Prize 1991) and Samuel F Edwards (b.1928; Boltzmann Medalist 1998) among others. For example, Flory devised a clever approximate treatment of the excluded volume problem, which was later cast into a field-theoretic formalism by Edwards; de Gennes exploited this insight to connect the problem with a magnetic phase transition in a certain limit (see Chapter 10). See Flory (1953), de Gennes (1979), Doi and Edwards (1986).

Colloids

Another example of entropy-dominated physics is the hard sphere colloid. Consider a suspension of micron-sized spheres, whose interactions are purely repulsive and of very short range. That is, centre-to-centre spacings less than one particle diameter are prohibited, but there is no force between spheres at larger separations. Then, all the microstates that are allowed at all (those with no overlaps between spheres) have precisely the same energy. Hence, from Eq.1, minimizing F amounts simply to maximizing S ; even the temperature T is immaterial.

What is the equilibrium state? This depends on the concentration of spheres, usually expressed through their ‘volume fraction’ ϕ , which is $\frac{4}{3}\pi R^3 N/V$, with N the number of spheres in volume V , and R their radius. A naive viewpoint of entropy maximization is that it corresponds to choosing a state of ‘maximum disorder’. But this viewpoint leads one astray here: for high concentrations obeying $0.545 \leq \phi \leq 0.74$ (nothing greater than 0.74 is possible for hard spheres), the state of highest entropy is found to be a regular lattice or ‘colloidal crystal’. Such a crystal has remarkable properties: for example its lattice planes cause scattering of visible light, analogous to the Bragg scattering of X-rays commonly used to probe the structure of atomic solids. This results in a iridescent, colourful appearance, called ‘opalescence’. (Opalescence is named after the appearance of gem opals, which are also regular arrays of hard spheres, that were once in a colloidal state but have since dried out.)

The first suggestion that hard spheres could crystallize in the absence of attractive interactions was made in the late 1930’s by John G Kirkwood (1907-1959) and the first ‘experimental’ evidence was in fact from the computer simulation pioneered in the late 1950s by Berni J Alder (b.1925, Boltzmann Medal 2001). A closely related issue, the occurrence of orientational ordering in hard-rod fluids, was resolved by Lars Onsager (1903-1976, Chemistry Nobel Prize 1968). For more detail of these developments, see

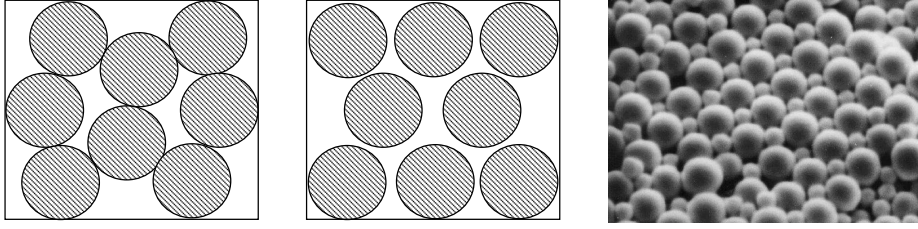


Figure 1. In a colloidal fluid phase (left), the mean particle density is uniform but individual spheres have little scope for exploration without requiring neighbours to move. In the colloidal crystal (centre), the decrease in entropy associated with a nonuniform mean density is compensated by a greater local volume that each particle can independently explore. (This is related to the fact that a higher density is achieved in a close packed crystal than in a random close-packed arrangement of spheres.) Right: a scanning electron micrograph of a dried colloidal crystal comprising spherical particles of poly(methylmethacrylate) of two sizes (radii 140 and 325 nm). Such crystals form over a few days from an initially fluid state. (Micrograph courtesy of Andrew Schofield, University of Edinburgh.)

Lekkerkerker (2000).

How can maximization of entropy lead to an ordered phase? To answer this, we can identify two distinct contributions to the entropy. The first one is the entropy associated with the mean particle density $\rho(\mathbf{r})$ which depends on position \mathbf{r} . This contribution, $S_1 = -k \int \rho \ln \rho d^3\mathbf{r}$ is maximum for a uniform mean density, $\rho = \text{constant}$, as arises in the fluid state. (Here k is Boltzmann's constant.) The crystal phase, in which ρ is strongly peaked at the lattice sites, loses heavily in terms of S_1 . But there is a second entropy contribution, which is much harder to calculate: a collective term S_C . This term reflects the difficulty particles have in locally avoiding their neighbours. In a dense colloidal fluid, few of the spheres can be displaced a significant distance without also requiring many neighbours to move. Put differently, the motion of the spheres in the fluid state is highly correlated; this means that the number of microstates (or distinct sphere configurations) actually available at a given ϕ is much less than S_1 might suggest. If, on the other hand, the spheres occupy an ordered lattice (on the average), then each has much more freedom to make small excursions from its lattice site, without interfering with its neighbours, than in a fluid of the same volume fraction. Qualitatively, this is because the long-range order of a crystalline lattice is very good at packing spheres efficiently, and more room remains for local exploration. So, S_C is much larger for the crystal than the fluid, if the density is high. The result is that when ϕ is high enough, $S_1 + S_C$ is larger for the crystal than for a fluid phase, so the crystal is stable. Similar arguments apply to more complex examples, such as a mixed suspension of colloidal spheres of different sizes (see Fig.1).

Although the hard sphere colloid is suspended in a solvent, for the purposes of evaluating the free energy F , the latter can almost be ignored. (It contributes a large but almost constant amount to the free energy.) Thus, for idealised hard spheres at a given volume fraction, the minimisation of F can be performed as if the spheres were in a vacuum; this was tacitly assumed above. Such calculations were first done in a different context, however – as an idealised model of simple atomic fluids. But in fact colloids are a much better approximation to hard spheres than atoms are;

hence experimental work on colloidal suspensions has (since about 1980) proven a fertile testing ground for classical theories of the liquid state and of crystallisation. As discussed below, by doing experiments on suitable mixtures (e.g. colloid + polymer) one can tailor the colloidal interactions to test these theories in more detail, for example by adding an attractive component to their interaction.

This ‘colloids as model atoms’ approach is reviewed comprehensively by Pusey (1991); see Anderson and Lekkerkerker (2002) for a more recent account.

Entropic Elasticity

The materials mentioned so far (gels, emulsions, colloids etc.) are all soft – but just how soft? What causes them to have any elasticity at all? Why is the static shear modulus not zero, as in a simple fluid?

The first satisfactory answer to this question was given for the case of ‘elastomers’, such as cross-linked rubbers and polymer gels. An elastomer consists of a network of polymer strands (each a random walk) linked together at junction points. If the gel is suddenly deformed at constant temperature, the random-walks strands must change their average shape: they become elongated along the stretching direction. The entropy of a set of deformed strands is lower than that of an undeformed set, for, by definition, the original random walk is the most random state possible. (In this case the naive argument, that maximum randomness equates to maximum entropy, turns out to be correct.) Hence the Helmholtz free energy F increases on applying a strain. The amount it increases is calculable in statistical models; in a small shear strain, characterized by a small strain angle γ (measured in radians) the free energy change is $\Delta F \simeq kTN\gamma^2$, where k is Boltzmann’s constant, and N is the number of network strands. Equating this stored free energy to $VG\gamma^2/2$ defines the shear modulus G ; this is of order kTN/V , or, kT times the number of ‘elastic degrees of freedom’ (N) per unit volume. Values for a typical polymer gel lie in the range $G = 10 - 10^4$ Pa, depending on the concentration of polymer and the amount of crosslinking. The upper end of this range lies several orders of magnitude below the shear modulus of, say, a typical metal. And, at the lower end, a value $G \simeq 10$ Pa represents a material whose elasticity resembles that of half-cooked egg-white.

These order-of-magnitude estimates for the modulus of elastomers stem from the pioneering work of Flory and others (Flory 1953). From the 1970’s onward, sophisticated quantitative theories for their elastic behaviour were developed to allow e.g., for the effect of ‘entanglements’. The latter arise from the fact that polymer chains cannot pass through each other; the result is an effective shortening of the network strands and an increase in their number.

Still smaller values ($G \leq 1$ Pa) can arise for the case of colloidal crystals. For these, a similar formula applies: $G \simeq kTN/V$ where N is the number of spheres. Compared with such a tiny modulus, even the force of gravity, acting on a sample a few millimetres across, is strong. A sample larger than this will usually collapse under its own weight, giving a nearly-flat meniscus in a test-tube, so that to the untrained eye it will appear to be a fluid (Pusey 1991).

In both elastomers and colloidal crystals, the smallness of the shear modulus G stems from the small number of elastic degrees of freedom (chains or spheres) per unit volume. In a conventional solid the elastic degrees of freedom correspond to atoms or small molecules, and the number of these objects per unit volume is vastly higher, giving G values of order 10^8 Pa or more. Note that similar arguments do not apply to

the bulk modulus K , which controls the free energy response to volume changes ΔV ($\Delta F = \frac{1}{2}K(\Delta V)^2$) in a system at fixed contents. The bulk modulus is dominated not by the polymers or colloids, but by the surrounding liquid, which is water, or some equally ‘normal’ molecular material (having, typically, $K \geq 10^8$ Pa). On the other hand, the experimenter can choose to study, instead of K , the ‘osmotic modulus’ \bar{K} . This is defined (and measured) by confining a soft material within a semipermeable cell of variable volume. In this case the system’s contents are not fixed: solvent can enter and leave, though the polymers or colloids cannot. The solvent contribution to the bulk modulus is thereby eliminated, and one finds that \bar{K} is again very small, roughly comparable to G .

Mixtures

In many real-world materials, both polymers and colloids are simultaneously present. Indeed, they may be accompanied by emulsion droplets, or surfactant aggregates (discussed further below), or yet further types of suspended object, in almost any combination. These components can interact in a strongly non-additive way: such a material is much more than the sum of its parts.

For example, suppose large colloidal spheres are mixed, in solution, with small polymers. The polymer coils cannot approach the impenetrable colloids too closely without becoming flattened out along the surface – a deformation which would cause them to lose entropy. To avoid this, the polymers tends to stay out of an ‘exclusion zone’ around each colloid; this also loses the polymers some entropy, though not as much. But now an even more economical arrangement is possible: this is to overlap the exclusion zones of different colloids. Such overlaps mean that the total ‘excluded volume’ (the volume that the polymers cannot get into without strongly deforming) is reduced; so the polymer entropy increases (Fig. 2). This argument shows that the free energy of the polymers is minimized by states in which the large colloidal spheres are close together. The effect of this is just as if there were an attractive force between the spheres. The range of this polymer-mediated ‘entropic attraction’ depends on the mean chain size; its strength, on the polymer concentration.

As mentioned previously, the physics of the colloidal particles in such a mixture is closely analogous to a system of inert atoms (such as argon). These have a strong repulsion when their electron clouds overlap, but a weak attraction at slightly larger distances. Indeed, by tuning the polymer concentration, analogues of the various phases of an atomic system can be mapped out experimentally. As well as the transition between a colloidal fluid and colloidal crystal (already described above), a ‘gas-liquid’ transition is now found, between two colloidal fluids having different volume fractions ϕ . By carefully varying the polymer size, studies have shown that the liquid state only exists when the attractive interactions are of long enough range. Such work is important for understanding colloids. It also illuminates a fundamental issue of molecular physics: the origin of the liquid state itself (Pusey 1991, Anderson and Lekkerkerker 2002).

Coulomb and Dispersion Forces

In many soft materials Coulombic, *i.e.*, electrostatic, interactions are vital: polymers, colloids and surfactants can all contain chemical groups which ionize when placed in water. Coulomb forces rank alongside entropy as a major determinant of physical

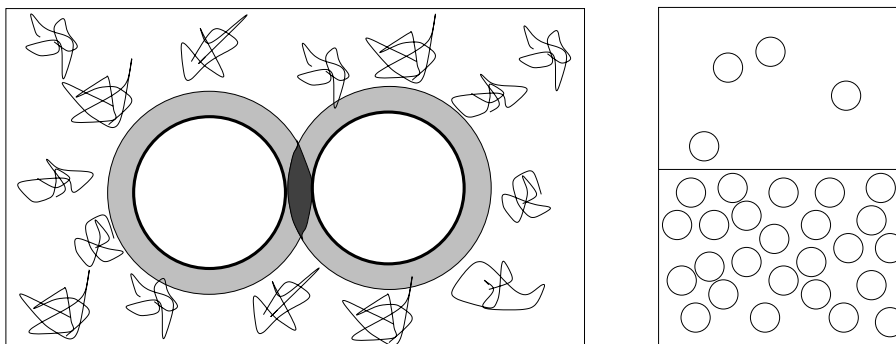


Figure 2. The “depletion force” in a colloid/polymer mixture. The polymers avoid the exclusion zone around each sphere (light shaded). By overlapping these areas, the total volume still available to the polymers can be increased by an amount equal to the dark shaded region. The resulting increase in polymer entropy causes a reduction in free energy of states in which the colloidal spheres are close together, that is, an effective attraction between spheres. This is called the depletion force. Like the attractive (van der Waals) force between inert gas atoms, it can cause a gas/liquid phase separation: in this context, coexistence of colloidal fluids of different volume fractions (right). The polymers (not shown) have a higher concentration in the phase with less colloid.

properties, at least in aqueous systems, and especially in biological ones. The same applies to dispersion forces – attractive interactions caused by the correlation of fluctuating dipole moments on different atoms or molecules.

Theories of simple ionic solutions (such as sodium chloride) were developed in the early 20th century. These were later combined with dispersion forces in theories of surface interactions by Lev D. Landau (1908-1968; Physics Nobel Prize 1962) and others; the resulting theory of colloidal interactions and its detailed experimental test are reviewed by Israelachvili (1985). By the end of the 20th century, the outstanding problems in this area mainly concerned the effects of strong correlations between charges; for example, current theories cannot adequately cope with ‘macroionic’ systems in which a polymer chain, or a colloid, carries hundreds of charges whose positions are thereby strongly correlated. In some regimes of strong charge correlation, even the basic sign of the interaction (attractive or repulsive) remains unresolved at the time of writing.

Dynamics

Even when the suspended objects are permanent (as for the colloidal and polymeric systems so far described), and all the same size, their dynamical behaviour can be somewhat complicated. In particular, the response of the material to a flow depends on how quickly its internal structure can reorganize to adapt to the changing shape of the sample.

The basic mechanism of this reorganization is Brownian motion: the jostling of a suspended object by continuous random collisions with the molecules of the surrounding fluid. Brownian motion is named after the botanist Robert Brown (1773-1858) who first observed it in pollen grains; it was explained by Albert Einstein (1879-1955; Physics Nobel Prize 1921) in 1905. (The effect was used by Jean Baptiste Perrin

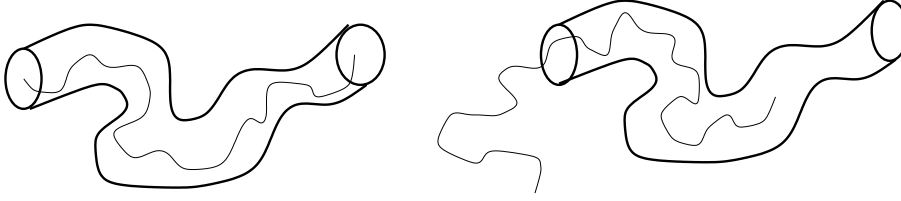


Figure 3. The tube model. In an entangled polymer system, a given chain (light curve) is densely enmeshed with its neighbours. The effect of the collisions with these neighbours is to confine the Brownian motion of the chain to the tube-like region depicted here. However, the chain can still disentangle itself by creeping along the tube axis (right). As it does so, it becomes enmeshed in a new tube (not shown) whose orientation is uncorrelated with the first. The process, called curvilinear diffusion, can be fully quantified within the model, and from this the stress memory function $\mu(t)$ can be found. (In fact, $\mu(t)$ is simply the fraction of the initial tube from which the chain has not escaped by time t .) In strong flows, the tube becomes deformed and this enhances the rate of disentanglement. These effects are quantified in the Doi-Edwards constitutive equation relating the state of stress $\sigma_{\alpha\beta}$ to the deformation history of the medium. A simplified version of this (called the ‘independent alignment approximation’ or IAA) reads $\sigma_{\alpha\beta}(t) = G \int_{-\infty}^t (d\mu(t-t')/dt') Q_{\alpha\beta}(E_{\gamma\delta}(t,t')) dt'$ where $Q_{\alpha\beta}$ is a specified tensorial function of the cumulative deformation tensor $E_{\gamma\delta}(t,t')$ between an earlier time t' and the present time t (whose logarithmic derivative is the strain rate tensor $\kappa_{\gamma\delta}$). The IAA equation is less accurate than the full equations of Doi and Edwards (1986), which are too complicated to reproduce here.

(1870-1942) to determine Boltzmann’s constant k ; for this he received the 1926 Physics Nobel Prize.) Brownian motion in soft condensed matter is complicated by the facts that (i) the suspended objects collide with each other as well as with the solvent; and (ii) for flexible objects such as polymers, collisions cause changes in shape, as well as in position, of these objects.

For example, polymers in solution, above a certain concentration, become hopelessly entangled with one another: the system resembles overcooked spaghetti (or, indeed, a ‘can of worms’). The flow behaviour of a polymeric fluid is dominated by the slowness with which these entanglements can be unravelled by Brownian motion. A mechanistic proposal for this, first put forward de Gennes, was developed by Edwards and Masao Doi (b.1948) into a simplified but quantitative theory of polymer viscoelasticity, called ‘the tube model’ (Doi and Edwards, 1986). Each polymer chain is envisaged as confined to a tube formed by entanglements with its neighbours; collisions keep it within the tube, but Brownian motion still allows it to creep slowly along the tube axis (Fig.3).

Within the tube model, one can explain what happens in an experiment like the following one. Take a soft polymeric material; suddenly shear it through a small angle γ which is then held constant; and measure the resulting shear stress, $\sigma(t)$, as a function of the time t since the strain was applied. For an elastic solid, such as the crosslinked polymer gel considered above, the stress forever obeys $\sigma = G\gamma$. For a viscoelastic material, one finds $\sigma = G\gamma\mu(t)$ where $\mu(t)$ is a decaying function of t . By convention $\mu(0) = 1$ so that G represents an ‘instantaneous’ elastic modulus, and $\mu(t)$ its decay. The tube model predicts, to reasonable accuracy, the shape of $\mu(t)$ and its dependence both on the mean chain length and on the state of entanglement.

Much more significantly, it also predicts the nonlinear viscoelastic behaviour of the system at large strains. In polymers this is characterized by a ‘shear thinning’ effect: if a large strain is applied (shearing through an angle γ that exceeds, say, 0.1 radian) then the material becomes, temporarily, even softer than before. More generally, the predictions of the tube model are summarized in a ‘constitutive equation’ which relates the state of stress at time t (formally the stress tensor $\sigma_{\alpha\beta}(t)$) to the history of deformations previously applied (formally the velocity gradient tensor $\kappa_{\alpha\beta}(t' < t)$). The Doi-Edwards constitutive equation has been very successful in predicting many phenomena previously unexplained. These include, for example, the observation that if a polymer solution is stirred with a rod, its top surface will climb up the rod. This is the exact opposite of what a Newtonian fluid does under the same conditions.

The tube model (and subsequent, more refined models based directly upon it) sets an enduring standard for what a good dynamical theory of soft condensed matter should aim to achieve. It offers a simplified but quantitative understanding of the relation between material properties and the underlying molecular disposition. To date, however, there is no other class of soft materials for which comparable success has been reported. One reason for this is that the tube model exploits the fact that, even under fairly strong flows, entangled polymer chains remain close to equilibrium on the mesoscopic scale that defines the tube. In many other soft materials, such as dense emulsions (mayonnaise) the same is not true: the strong flow regime brings strong departures from equilibrium even at a local scale. The experimental and theoretical situation is comprehensively described in Larson (1999).

Self-Assembly

Let us now consider the case when the mesoscopic objects in a fluid are not permanent, but transitory in character, such as can arise by the ‘self-assembly’ of small molecules into large clusters.

For example, a simple detergent molecule (or soap) has a hydrocarbon tail, which repels water, capped with a water-loving head group. This type of molecule is called an ‘amphiphile’; their propensity for self-assembly and for adsorption at surfaces fascinated Irving Langmuir (1881-1957, Chemistry Nobel Prize 1932). When placed in water, such molecules will spontaneously form clusters, or ‘aggregates’, that minimize the contact area between the tails and the surrounding liquid. These aggregates are transitory, since Brownian motion is enough to break them. (In many cases they flicker in and out of existence on a microsecond timescale.) Depending on the relative sizes of head and tail, the optimal packing can be a small sphere (called a micelle), a long flexible cylinder (giant micelle), or a flat sheet (bilayer). Giant micelles are objects similar to polymers, but their transitory nature leads to more complex dynamics (see Cates and Candau 1990): reversible splitting and re-forming of the chains modifies the process of Brownian disentanglement. And in some systems, the micelles can become branched, forming a fluid network of one-dimensional, cylindrical tubules. These and other states of organization for cylindrical aggregates are shown in the schematic ‘phase diagram’ of Fig.4.

Turning now to the case of an extended bilayer (Fig.5) this can reconnect itself topologically to form a multiply-connected, sponge-like film on which the detergent molecules live as a two dimensional fluid. There is a surprising, and deep, analogy between this film and the interface between ‘up’ and ‘down’ spins in a ferromagnetic solid. The bilayer film divides space into two domains which are of equal volume at

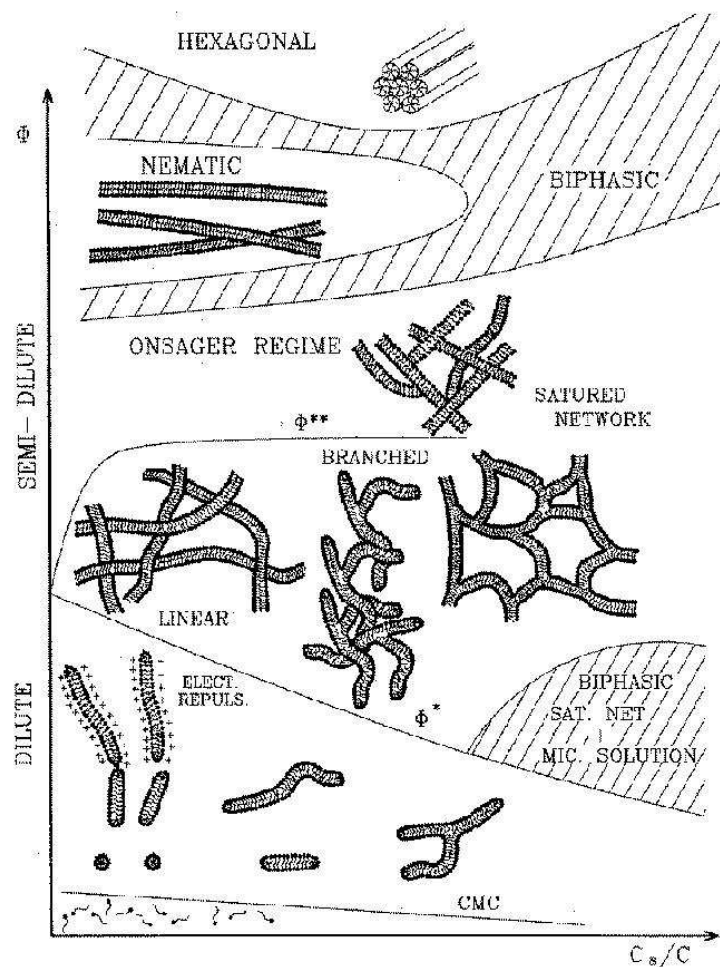


Figure 4. Schematic phase diagram of cylindrical aggregates in water. Regimes of different organization are sketched on the $C_s/C, \Phi$ plane, where C_s/C is the molar ratio of salt to amphiphile, and Φ is the volume fraction of amphiphile. Shaded areas are where the equilibrium state of the system is represented by coexistence of different phases (compare the colloidal vapour/liquid coexistence shown in Fig.2). Lines marked Φ^* and Φ^{**} denote gradual crossovers between a dilute regime, the so-called 'semi-dilute' regime of entangled (and/or branched) flexible cylinders, and an 'Onsager' regime of entangled semi-stiff cylinders, respectively. At still higher concentrations, two liquid crystal phases (nematic and hexagonal) arise. For ionic detergents, electrostatic interactions are important at low C_s/C and low Φ , as indicated. Below the line marked CMC (at very low Φ values) the detergent is present as a molecular solution; there is no longer significant aggregation. (Figure courtesy of François Lequeux and Jean Candau.)

high detergent concentrations (the ‘symmetric sponge’, analogous to a paramagnet) but of unequal volume at lower concentrations (the ‘asymmetric sponge’, analogous to a ferromagnet). In some bilayer systems these two distinct phases, both of which are isotropic fluids, are connected by a phase transition where various anomalies, for example in turbidity and light scattering, have been observed.

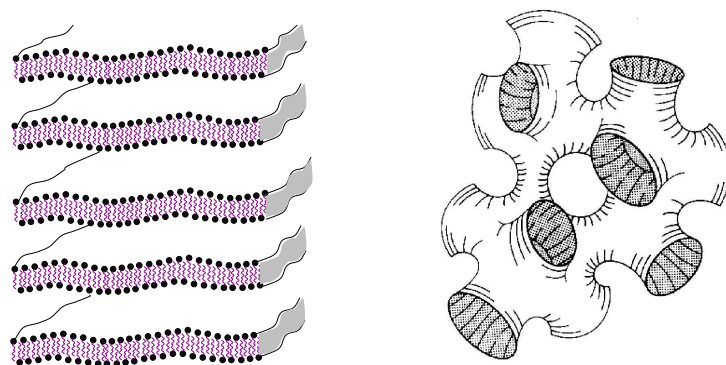


Figure 5. States of organization for bilayer films. Both outer surfaces of such a film are coated with head-groups of the amphiphilic molecules; these are exposed to water and protect the inner regions where the tails reside. In the lamellar phase, extended, roughly flat, bilayer sheets form a stack (left); in the sponge phase (right) these fuse into a single surface of complex topology. (Drawing: courtesy Gregoire Porte.) Such a bilayer surface divides space into two distinct solvent domains, which may or may not have equal volumes (symmetric or asymmetric sponge).

The same local structures of cylindrical or sheet-like aggregates can also arise in ordered phases, such as a regular array of cylinders, or a regular stack of sheets; both are liquid crystals. The cylinders show periodic order (crystallinity) in two directions but fluid-like behaviour in the third, which lies along the cylinder axis. In the bilayer case, extended two-dimensional fluid films adopt a pack-of-cards arrangement, with periodic order in the third (stacking) direction. This so-called ‘lamellar’ phase is actually the structure of wetted soap slime, mentioned previously; its very sliminess stems from the ease with which the layers can slide over one another (just like a deck of cards).

In the case of cylindrical micelles, a third possibility exists, called the ‘nematic’ liquid crystal. In this phase, the micelles all point in roughly the same direction, spontaneously breaking the rotational symmetry of an isotropic fluid, but without long-range positional order in any direction.

All these liquid crystal phases have special kinds of elasticity which reflect their unusual state of order; their properties have been explored by Landau, de Gennes and Onsager among others (see de Gennes 1972). And, just as in the polymeric and colloidal systems described above, entropy and thermal fluctuations play an important role. For example, in the lamellar liquid crystal, Brownian motion causes each fluid bilayer to wobble slightly around its mean position. These fluctuations are restricted by the fact that each bilayer cannot cross its neighbours. The more flexible the bilayers, and the closer they lie together, the larger is this entropic penalty. So, while a stack of very flexible bilayers is easily bent, it is much harder to compress (even if the solvent is allowed to escape – an ‘osmotic compressibility’ test). This is, incidentally, why the

onion-like bilayer structures shown in Fig. 6 (and discussed below) are polyhedral, not spherical, in shape: although a sphere minimizes curvature, a polyhedron, by making the best use of space, minimizes compression.

The osmotic compressibility and other properties of self-assembled phases, can in many cases, be quantitatively related to the local elastic constants of the aggregates that they contain. These elastic constants are few in number and their control of macroscopic properties represents a striking example of the universality concept mentioned in the introduction. This key insight was the basis of pioneering work by Wolfgang Helfrich (b.1932) who applied these ideas in the 1970's first to lipid membranes arising in a biophysical context; the approach is reviewed, alongside many of the subsequent developments outlined above, by Gompper and Schick (1994). Since the early 1990s, the study of self-assembled amphiphilic systems increasingly embraced biophysical applications, with simplified lipid bilayers extensively studied as models for cell membranes; such work is reviewed in Lipowsky and Sackmann (1995).

Fractal Aggregates and Colloidal Gels

A somewhat different type of spontaneous aggregation occurs in colloidal suspensions when attractive forces are present between colloidal particles (sticky spheres). The particles can adhere to form tenuous threadlike structures, typically 'fractal' in nature. A well-known example is the domain structure in a ferromagnet at the critical point. Here regions of positively and negatively aligned spins form fractal patterns, so that, as long as one does not look closely enough to resolve individual spins, it is impossible to tell from a picture of the spin pattern what magnification or resolution has been used. Similar remarks apply to photographs of colloidal aggregates formed, for example, by suddenly changing temperature or pH to ensure that a strong attraction (e.g. from dispersion forces) arises between colloidal particles that were previously repulsive to one another (e.g. because of a Coulomb repulsion).

The realisation that fractal concepts could be used to describe colloidal aggregation caused an outburst of interest in the problem among physicists in the 1980s. This followed from pioneering work of Thomas A Witten (b.1944), who first recognised that the nonequilibrium fractal structures seen in simple models of aggregation were signatures of a critical phenomenon analogous to that found at continuous phase transitions (see Chapter 10). It is notable that computer simulation played a key role in this work; direct comparison between experimental and simulated data became the main test of theory in this area. These developments are reviewed by Vicsek (1989).

Whenever these fractal aggregates link up into a continuous web, a network arises, called a 'colloidal gel'. Depending on the strength of the interactions, the aggregates may or may not gradually break up and reconnect by Brownian motion; often, they can easily be broken apart by an applied stress. This can lead to a different type of viscoelasticity from that described above for polymers. Here the material remains an elastic solid almost indefinitely ($\mu(t) = 1$) so long as the applied stress $\sigma = G\gamma$, remains below a certain threshold. Only if this 'yield stress' is exceeded, does the material begin to flow. To add to the complication, the yield stress itself can slowly evolve with time in a process called 'ageing'.

At the time of writing, the formation, flow and aging behaviour of colloidal gels remains relatively poorly understood – partly because, for the gel to flow at all, the bonds cannot form in a completely irreversible manner as simple aggregation models

assume; see e.g., Haw and Poon (1997).

Flow-Induced Phase Transitions

Both amphiphilic and colloidal aggregates can show a strong coupling between their state of organization and the state of flow in the material. This can have spectacular consequences. For example, in some cases it is possible to convert an isotropic fluid, containing a spongelike amphiphilic bilayer, into a lamellar liquid crystal, merely by a light shaking of the sample in a test tube. Similarly, many colloidal crystals can be rapidly converted to a fluid state by slight shearing. These are both ‘flow-induced phase transitions’. (The term ‘phase transition’ means an abrupt change in the response of a system, or the functional form of this response, under a smooth change in parameters such as temperature or – here – flow rate: see Chapter 10.)

In the simplest cases, the shear induces a transformation which could also have been made by changing a thermodynamic variable such as temperature or pressure. Indeed, in both of the above examples, the same effect could be achieved by changing the concentration slightly, rather than applying the shear. Several flow-induced transitions are now well understood in these terms.

In a second class of systems (including giant micelles) an abrupt transition from one state of flow to another, as a function of flow rate, is required by the constitutive equation. This ‘intrinsic’ flow instability may or may not be accompanied by a change of thermodynamic state, for example to a hexagonal or a nematic liquid crystal.

In a third class of systems, the application of a flow produces a state of organization which is entirely new. A spectacular example is when a lamellar liquid crystal is subjected to prolonged steady shear (Fig.6). Rather than remain as a regular stack, the layers slowly reorganize into closed shells of spherical topology (but polyhedral shape) nested one inside another, forming an array of ‘onions’. (Each onion is typically a few microns across, and contains hundreds of layers.) This transformation is reversible: by reducing the shear-rate, the previous structure is recovered. However, if shearing suddenly ceases altogether (so there is no longer a steady input of energy from outside) the onions cannot revert to their previous structure at all quickly; in some cases, they are stable for months. This provides an interesting technology for encapsulating small molecules, such as pharmaceuticals, which can be added to the mix before the onions are made.

Another example of a flow-induced phase transition occurs in solutions of giant micelles, at concentrations below the onset of entanglements. Such a solution is barely viscoelastic, but when sheared slowly and for a long period, it transforms into a new, gelatinous state. Theoretically, one expects shear to have a strong effect in a system like this, but only when the shear rate $\dot{\gamma}\tau \geq 1$, where τ is the longest relaxation time observable in the system at rest. (Here, τ is the rotational relaxation time of the micelles: micro- or milliseconds.) But in this case the shear rate required is tiny: $\dot{\gamma}\tau \leq 10^{-3}$; this is far from understood.

The first systematic experimental studies of flow-induced phase transitions in self-assembled materials were carried out in the 1980s (Rehage and Hoffmann 1991), whereas the onion transition was not discovered until later (Diat, Roux and Nallet 1992). Despite much theoretical effort, there had been relatively little progress in understanding these transitions except for a few limiting cases, some of which are reviewed by Larson (1999).

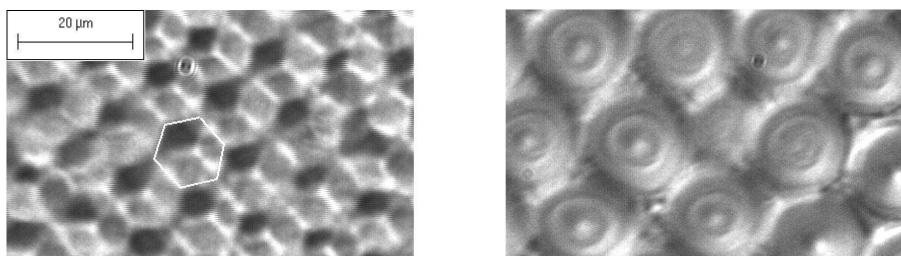


Figure 6. An onion texture in a sheared lamellar phase, viewed with differential interference contrast microscopy. Immediately after prolonged slow shearing, the close-packed onions have polyhedral shapes (left). It is hard from such a picture to see where one onion ends and the next begins, but an example is picked out in white. If some extra solvent (water) is now added, the onions swell significantly in size and become more separated. Their spherical topology is now more clearly visible. (Figure courtesy of Mark Buchanan.)

Jamming and Granular Media

Under some conditions, a suspension of hard-sphere colloids can undergo a flow-induced phase transition from a relatively free-flowing phase into a ‘jammed state’. This appears to be related to the physics of traffic jams: on a crowded freeway, there is a mean speed above which traffic cannot flow freely. Even if all drivers wish to go faster than this, they cannot, because the flow is unstable, and small fluctuations lead to spontaneous jams.

A classical experiment along these lines can be performed in the kitchen: place a tablespoonful of starch granules (corn starch or custard powder) in a cup, and add water drop by drop, until the material is only just properly wet. Now stir with a spoon. If the composition is just right, the suspension will flow almost without resistance, so long as the spoon is moved slowly. But an attempt at rapid stirring is completely frustrated – the whole thing sets into a solid lump. Work in the late 1990s began to illuminate such processes (Fig.7), although the physics of the situation is far from clear.

The nature of the jamming transition in colloids also suggests an intriguing connection with another class of easily-jammed materials: granular media. These include dry powders, such as sand. There is a continuous spectrum connecting dry powders (via slurries and pastes) all the way to the colloidal state. Across this spectrum, some common tools began to emerge during the 1990s, for example, a characterization of local geometry based on ‘force chains’ of strong local contacts. But a truly unified theoretical framework remains lacking.

Arrested Dynamics

Many soft materials, such as the deformed fluid droplets in a dense emulsion, or the onions in Fig. 6, are trapped in an arrested state, far from true equilibrium, and yet close enough to a metastable minimum of free energy to allow thermodynamic ideas to be employed locally, or for short time scales. At longer time scales, such materials can exhibit very slow relaxation processes; in several cases, no matter how long one observes the system, its properties continue to evolve.

From the 1970s onward, broadly analogous behaviour to this had been seen

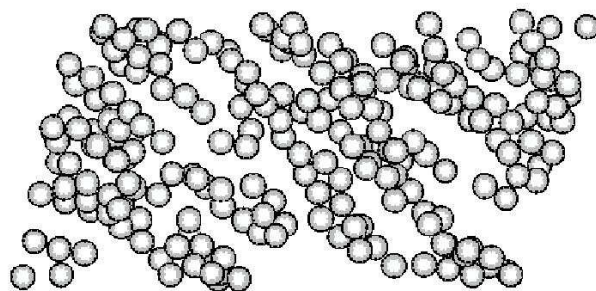


Figure 7. The jamming transition in a sheared colloid. The data are from a computer simulation of a hard sphere colloidal suspension at $\phi = 0.54$ which has been strained to $\gamma = 0.22$. Shown in the figure are only those spheres which have come into very close contact ($\leq 10^{-5}$ radius) with at least one neighbour. As can be seen from the figure, the contact geometry is strongly anisotropic and suggests the formation of ‘force chains’ running top left to bottom right. Similar force chains have been reported in granular materials. (The simulation is by J Melrose, Cavendish Laboratory; the figure is courtesy of him.)

in other areas of condensed matter, particularly in disordered magnets called ‘spin glasses’ (see Chapter 11.3). This work was itself partly inspired by earlier experimental studies of ‘structural glasses’ that arise by supercooling of molecular fluids, such as glycerol, into the vitreous regime. In the 1980s, dense colloidal suspensions were themselves shown to be structural glasses, in the sense that the particles become trapped close to fixed positions although these do not form an ordered lattice (Pusey 1991). In the 1990s it was proposed that that glass paradigm could explain a wider range of arrested dynamics in soft condensed matter, such as that of dense emulsions or textured liquid crystalline phases (e.g. onions) in which one can expect a slow evolution of the system through a sequence of metastable, near-equilibrium states. It was also proposed that the jamming transition might be related to a transition from fluid to glass caused by the imposition of a stress. These and other ideas are explored in a recent proceedings (Cates and Evans 2000).

Phase Transition Kinetics

A simpler form of metastability than that found in glasses arises in a supercooled vapour, for example. In such cases the system resides in one of a small number of free energy minima, corresponding to different thermodynamic phases, even though its free energy F could be lowered by moving to another one. The transition may finally proceed, for example, via nucleation of a small droplet of the preferred phase. A different mechanism arises when, because of a sudden change of parameters (such as a temperature change or ‘quench’) a system which was originally at a free energy minimum suddenly finds itself at or near a maximum, and starts to evolve accordingly. An example is when a stable mixture of two fluids is cooled, and starts to demix by a process called ‘spinodal decomposition’ (Bray 1994).

The demixing kinetics of simple liquids and solids is a well-established field of condensed matter physics in its own right. In metallic alloys, for example, there is a reasonable empirical knowledge of how the process affects the resulting microstructure. Despite extensive investigations, a similar understanding of ‘process pathways’ in soft

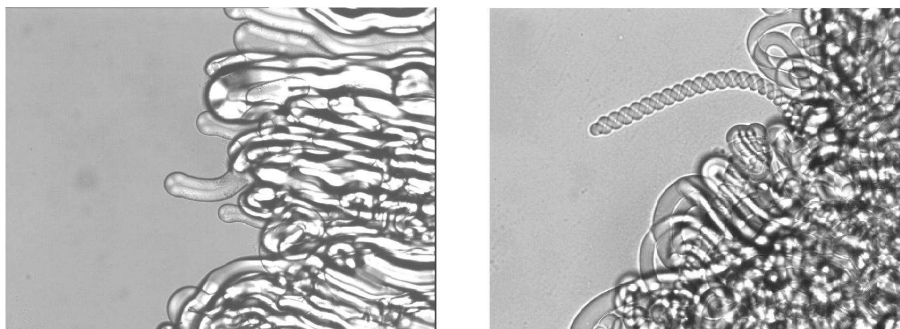


Figure 8. The myelinic instability of a dissolving lamellar phase. In both pictures, the lamellar phase is on the right; water is on the left. As the two phases mix, the interface broadens and myelinic figures are seen. These are long tubular fingers formed from concentric cylindrical bilayers. As time passes, the myelins can become more exotic in form, such as the double helix shown on the right. (Figure courtesy of Mark Buchanan.)

condensed matter remains lacking, although important progress was made in the late 1990s, at least of one important class of systems (colloid-polymer mixtures); this is reviewed by Anderson and Lekkerkerker (2002). For example, a colloid or paste (be it paint, shampoo, or tomato sauce) is useless if it prematurely separates into a solid block of material with a layer of solvent on top. Whether it will do this depends on its microstructure; and that in turn depends on its process history.

Equally interesting, and less well-studied in other branches of condensed matter physics, is the reverse process. How do initially separated phases mix, if thermodynamic conditions are changed to favour this? For example, a bilayer liquid crystal, as it dissolves into excess water, can show various instabilities. An example is the ‘myelinic’ instability in Fig.8, named after the myelin sheaths which surround nerve cells in the body, and which the observed finger-like patterns closely resemble. This has still not been systematically studied or explained, despite having been first reported in the mid 19th century (Virchow 1854). One can earnestly hope for quicker progress in the next century.

Relation To Other Disciplines

Soft condensed matter physics forms part of few undergraduate curricula, and remains a minority (though a growing) interest among professional condensed-matter physicists. Among the latter, it has an undeserved reputation for being a ‘messy’ subject, meaning perhaps that, in many soft materials, chemistry as well as physics must be used before a complete understanding is obtained. This is true, but the physical themes of large thermal fluctuations, constrained Brownian motion, and entropic elasticity recur in system after system. These provide a unifying conceptual framework within which more specific chemical features can then be addressed. Although materials scientists, chemists and chemical engineers have had a strong role to play, the recognition of such underlying universalities, and the building of the aforementioned framework linking experiment firmly into statistical mechanics, was arguably the distinctive contribution of physicists to the study of soft condensed

matter during the second half of the 20th century.

What about biology? The 1980s and 1990s saw an increasing dialogue between soft matter physicists and biologists (Lipowsky and Sackmann 1995). One difference between soft-matter physics and biology is inescapable, however. Physicists are trained to consider the generic features of any problem, and then apply the resulting insights to other situations that are broadly similar but different in detail. But biological structures have been honed by evolution so that the physical exception is (often) the biological norm. In such circumstances, existing conceptual tools will need to be modified and new ones invented; this vista for future research extends far into the 21st century.

Soft Matter and Science Politics

The physics of soft condensed matter has posed (and continues to pose) stimulating challenges to experimentalists, theorists, and computer simulators alike. It is all the more appealing because it addresses the properties of materials that we encounter every day: materials we eat, rub on our skin, decorate our homes with, and (to some extent) are ourselves made from. The intellectual and scientific curiosity that this arouses has, I hope, been partly conveyed in this historical survey. Moreover, a deeper understanding of these properties, and how to control them, can yield important rewards.

The study of soft condensed matter addresses familiar materials; and familiarity, it is said, breeds contempt. Perhaps this is why, at least during the 1980s and 1990s, the non-scientific press often seemed more interested in generating humorous but inaccurate headlines ('mad scientists spend government cash shaking tomato sauce') than conveying to their readers any idea of what the research entailed. A disparaging attitude among colleagues in more 'mainstream' areas of research has also been detectable at many times during that period. In contrast, members of the public have shown delight in learning that professional scientists (as well as themselves) still do not understand why the tomato sauce sometimes just won't come out of the bottle. And few of them doubt that solving this small problem, alongside a thousand larger ones, could make their lives in the 21st century a little easier.

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